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(54) **CERAMIC WITH OXIDISABLE LAYER**

**KERAMIK MIT OXIDIERBARER SCHICHT**

**CERAMIQUE COMPORTANT UNE COUCHE OXYDABLE**

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• **LUTHRA, Krishan, Lal**  
**Schenectady, NY 12309 (US)**

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(74) Representative: **Szary, Anne Catherine, Dr. et al**  
**GE London Patent Operation,**  
**Essex House,**  
**12-13 Essex Street**  
**London WC2R 3AA (GB)**

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(73) Proprietor: **GENERAL ELECTRIC COMPANY**  
**Schenectady, NY 12345 (US)**

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**EP-A- 0 310 043** **EP-A- 0 427 294**  
**US-A- 5 683 824**

(72) Inventors:  
• **WANG, Hongyu**  
**Niskayuna, NY 12309 (US)**

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## Description

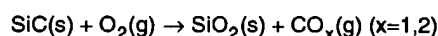
[0001] This invention was made with government support under Contract No. NAS3-26385 awarded by NASA. The government may have certain rights in the invention.

## BACKGROUND OF THE INVENTION

[0002] The invention relates to an article that includes a silicon-containing substrate and an intermediate layer/coating with an external barrier coating such as a protective environmental/thermal barrier coating (E/TBC).

[0003] Silicon-containing substrates have been proposed for structures used in high temperature applications, such as in heat exchangers and advanced internal combustion engines. Silicon-containing substrates are also used in gas turbine engines. Higher operating temperatures increase the efficiency of gas turbine engines. Silicon-based composite ceramics have been proposed as materials for applications in combustors for supersonic commercial airplanes. However, in many applications involving water-containing environments, a silicon-based substrate will recede and lose mass because of the formation of volatile species, such as silicon hydroxide  $[\text{Si}(\text{OH})_4]$ . The recession rate due to the volatilization or corrosion is often unacceptably high so that an external barrier coating such as an environmental/thermal barrier coating (E/TBC) with high resistance to such environments is required.

[0004] The external barrier coating can be an environmental/thermal barrier coating (E/TBC) that comprises a chemically stabilized zirconia, such as yttria stabilized zirconia. These coatings are capable of preventing the substrate materials from being in direct contact with environmental oxygen that diffuses through the coatings fairly rapidly and reaches the underlying silicon-containing substrate. Oxidation of the silicon-containing substrate involves the formation of various gaseous products. For example, the following equations demonstrate the attack on silicon carbide (SiC) and silicon nitride ( $\text{Si}_3\text{N}_4$ ):



[0005] The form of the gaseous products is dependent on the oxygen partial pressure in the system. These gaseous species have low solubility and diffusivity in silica ( $\text{SiO}_2$ ) and in other oxides, which causes them to be trapped at the external coating/substrate interface to form voids. The pressure of the gases in the voids can be sufficiently high at elevated temperatures to cause bursting. Voids can also interconnect to form large unbounded interfacial regions that result in coating spallation.

[0006] Thus, there is a need to prevent formation of gaseous oxidation products at an interface region between an environmental/thermal barrier coating (E/TBC) and a silicon-based substrate.

[0007] US-A-5683824 discloses a coated ceramic member which includes a silicon nitride- or silicon carbide-based ceramic base material, a silicon nitride or silicon carbide film formed on the base material by CVD, and an oxide film formed on the film of CVD.

[0008] EP-A-0310043 discloses an oxidation resistant, high temperature thermal cycling resistant coated ceramic article for ceramic heat engine applications. The substrate is a silicon-based material, i.e. a silicon nitride- or silicon carbide-based monolithic or composite material. The coating is a graded coating of at least two layers: an intermediate  $\text{AlN}$  or  $\text{Al}_x\text{N}_y\text{O}_z$  layer and an aluminum oxide or zirconium oxide outer layer. The composition of the coating changes gradually from that of the substrate to that of the  $\text{AlN}$  or  $\text{Al}_x\text{N}_y\text{O}_z$  layer and further to the composition of the aluminum oxide or zirconium oxide outer layer. Other layers may be deposited over the aluminum oxide layer.

[0009] EP-A-0427294 discloses a silicon carbide member manufactured by depositing a silicon carbide coating on a substrate of silicon carbide containing free silicon by chemical vapor deposition. By gradually reducing the content of free silicon of the coating such that the coating is made of silicon carbide containing free silicon at the interface with the substrate, but of silicon carbide containing no free silicon at the outer surface, the coating is firmly bonded to the substrate, undergoes little thermal stress and is resistant against cracking and separation upon thermal cycling.

## SUMMARY OF THE INVENTION

[0010] The present invention provides an article that prevents or substantially diminishes the formation of gaseous products at a coating substrate interface. The invention is an article that comprises a silicon-containing substrate and at least one external environmental/thermal barrier coating. The external environmental/thermal barrier coating(s) is permeable to diffusion of environmental oxidant and the substrate is oxidizable by reaction with the oxidant to form at

least one gaseous product. The article comprises an intermediate layer/coating between the silicon-containing substrate and the external environmental/thermal barrier coating(s) that is oxidizable to a nongaseous product by reaction with the oxidant in preference to reaction of the silicon-containing substrate with the oxidant, wherein (i) the intermediate layer/coating is silicon or a silicon containing alloy or (ii) the intermediate layer/coating has a final strata that consists of silicon or a silicon-containing alloy

[0011] In another aspect, the invention relates to a method of forming an article, comprising forming a silicon-containing substrate that is oxidizable by reaction with oxidant to form at least one gaseous product and applying an intermediate layer/coating onto the silicon-containing substrate, wherein the intermediate layer/coating is oxidizable to form a nongaseous product by reaction with the oxidant in preference to reaction of the silicon-containing substrate with the oxidant, wherein (i) the intermediate layer/coating is silicon or a silicon containing alloy or (ii) has a final strata that consists silicon or a silicon containing alloy.

#### BRIEF DESCRIPTION OF THE DRAWINGS

##### [0012]

FIG. 1 is a photomicrograph for an article without an intermediate layer/coating;

FIG. 2 is a photomicrograph for an article with an intermediate layer/coating; and

FIG. 3 is another photomicrograph for an article with an intermediate layer/coating formed by silicon melt infiltration.

#### DETAILED DESCRIPTION OF THE INVENTION

[0013] According to the invention, an article comprises a silicon-containing substrate and an intermediate layer/coating. The invention further comprises at least one external environmental/thermal barrier coating(s) applied to the intermediate layer/coating. The intermediate layer/coating prevents the formation of gaseous products that form voids at the external environmental/thermal barrier coating-substrate interface. The voids can burst and can interconnect to form large unbounded interfacial regions. This can result in coating spallation and depreciated bonding between the silicon-containing substrate and the external environmental/thermal barrier coating(s).

[0014] According to the invention, an intermediate layer/coating is provided to reduce the gaseous products that would otherwise be emitted by reaction of the silicon-containing substrate with oxidants. The intermediate layer/coating preferentially reacts with oxidants to form non-gaseous products.

[0015] The intermediate layer/coating preferentially react with oxidants to form a non-gaseous product and includes elemental silicon (Si) and silicon-alloys such as silicon aluminum (Si-Al), silicon chromium (Si-Cr), silicon magnesium (Si-Mg), silicon calcium (Si-Ca), silicon molybdenum (Si-Mo) and silicon titanium (Si-Ti). The silicon-alloy is chosen so that permeability of oxidants through the oxidation product of the alloy is low (compared to silica) in order to prevent rapid oxidation of the intermediate layer/coating. Preferably, the intermediate layer/coating consists of silicon.

[0016] The thickness of the silicon intermediate layer/coating can be estimated based on the data of B. E. Deal and A. S. Grove, "General Relationship for the Thermal Oxidation of Silicon," *J. Appl Phys.*, 36 [12] 3770-78 (1965) on the oxidation of silicon. The results are summarized in Table 1. The calculations were performed for silicon oxidation in dry oxygen ( $O_2$ ) environment, assuming water ( $H_2O$ ) in the combustion gas will not permeate through the oxide coating. The time for oxidation at high temperatures (1100-1400°C) is 4,500 hours. Therefore, if a dense uniform layer/coating of silicon can be applied, a coating thickness of about 0.5 mil (12.7 $\mu$ m) will suffice for a 4,500 hot hour application below about 1400°C. A thickness of about 1-2 mil, however, may be more practical.

Table 1

Thickness of Silicon Oxidized at Different Temperatures for 4,500 Hours			
Temperature (°C)	$O_2$ Diffusivity ( $\mu m^2/hr$ )	Thickness of $SiO_2$ ( $\mu m$ )	Thickness of Si formed oxidized ( $\mu m$ )
1100	0.027	11.0	4.8 (0.1 mil)
1200	0.045	14.2	6.3 (0.2 mil)
1300	0.075	18.4	8.1 (0.3 mil)
1400	0.136	24.7	10.9 (0.4 mil)

[0017] Suitable silicon-containing substrates include silicon carbide (SiC) and silicon nitride ( $Si_3N_4$ ), as well as silicon alloys such as niobium silicon alloys, molybdenum silicon alloys and the like. The silicon-containing substrate can be

a monolith or composite. A composite can comprise a reinforcing fiber, particulate or whisker and a silicon-based matrix. Exemplary fibers, particulate or whiskers are silicon carbide-containing, carbon-containing, silicon-containing, or mixtures thereof. The fibers, particulate or whiskers optionally can have at least one coating, such as a silicon nitride, silicon boride, or silicon carbide coating. The matrix can be processed by melt infiltration (MI), chemical vapor infiltration (CVI) or other technique. Exemplary silicon-containing substrates include a monolithic silicon carbide (SiC) and silicon nitride ( $\text{Si}_3\text{N}_4$ ), a silicon carbide (SiC) fiber-reinforced silicon carbide (SiC) matrix composite, carbon fiber-reinforced silicon carbide (SiC) matrix composite, and a silicon carbide (SiC) fiber-reinforced silicon nitride ( $\text{Si}_3\text{N}_4$ ) composite. The preferred substrate comprises a silicon carbide (SiC) fiber-reinforced silicon-silicon carbide (Si-SiC) matrix composite processed by silicon melt infiltration.

**[0018]** Exemplary of external environmental/thermal barrier coatings are chemically stabilized zirconias, alumina, and alumina silicate with or without bond coatings. Chemically stabilized zirconias include yttria stabilized zirconia, scandia stabilized zirconia, calcia stabilized zirconia, and magnesia stabilized zirconia. Exemplary bond coats are mullite, modified mullite,  $\text{MCrAlY}$  where M is nickel, iron, cobalt, nickel and cobalt, and mixtures thereof. Modified mullite comprises mullite and a modifier component. Modifier components for mullite include alkaline earth aluminosilicate, with the formula  $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , where M is an alkaline earth element. Preferred modifier components of the formula  $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  include barium feldspar ( $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), strontium feldspar ( $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), and combinations of barium feldspar ( $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), and strontium feldspar ( $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). Preferably, the alkaline earth aluminosilicate has a monoclinic celsian crystalline phase. Most preferred aluminosilicates include  $(\text{BaO})_{0.75}(\text{SrO})_{0.25} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  referred to as BSAS,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  referred to as CAS and  $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . Other suitable modifiers include materials referred to as NZP's such as  $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ,  $\text{Ba}_{1.25}\text{Zr}_{0.5}\text{P}_{5.5}\text{Si}_{0.5}\text{O}_{24}$ ,  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4(\text{PO}_4)_6$  and  $\text{Ca}_{0.6}\text{Mg}_{0.4}\text{Sr}_4(\text{PO}_4)_6$ . Other preferred modifier components include yttrium silicates, calcium aluminates including  $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ , aluminum titanates including  $\text{Al}_2\text{O}_3 \cdot \text{TiO}_3$ , cordierite ( $2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ), fused silica ( $\text{SiO}_2$ ) and silicon (Si). These materials are also chemically compatible with mullite.

**[0019]** The modifier components may be added to the modified mullite coating in a percent volume range between about 5 to about 50. Preferably, the modifier component is present in about 10 to about 30 volume percent of the modified mullite coating and most preferably in about 15 to 25 volume percent.

**[0020]** Preferably, the intermediate layer/coating is silicon and is applied between a silicon carbide (SiC) or silicon nitride ( $\text{Si}_3\text{N}_4$ ) substrate and an external environmental/thermal barrier coating such as yttria-stabilized zirconia with a modified mullite bond coating.

**[0021]** The article of the invention may be used as a discrete composite article such as a gas turbine engine part.

**[0022]** When the intermediate layer/coating is silicon, the silicon preferentially reacts with oxygen to form a non-gaseous product to reduce the formation of voids that would otherwise deteriorate the bond between silicon-containing substrate and the environmental/thermal barrier coating(s). Additionally, the resulting silicon oxide ( $\text{SiO}_2$ ) has a low oxygen permeability. Hence, the intermediate layer/coating acts as a protective barrier that deters permeation of oxygen into the substrate layer by at least two mechanisms. The source of gas generation is eliminated and voids are prevented that would otherwise accumulate at the interface between the external coating and silicon-containing substrate. Further, the product of the preferential reaction provides a barrier to permeation of unreacted oxygen into the silicon-containing substrate.

**[0023]** A silicon intermediate layer/coating can provide additional advantages. Silicon has a coefficient of thermal expansion (CTE) similar to that of silicon carbide (SiC) and mullite. Hence, an intermediate silicon layer/coating can minimize thermal stresses between the environmental/thermal barrier coating(s) and the silicon-containing substrate when used in combination with a silicon carbide (SiC) substrate and a mullite bond coating or external environmental/thermal barrier coating(s). A preferred article of the present invention comprises a silicon-containing substrate that is a melt infiltrated silicon-silicon carbide (Si/SiC) matrix reinforced with silicon carbide (SiC) fibers and an intermediate layer/coating that comprises silicon. An external environmental/thermal barrier coating(s) such as a bond coat (for example, mullite,  $\text{MCrAlY}$  where M can be nickel, iron, cobalt, and mixtures thereof) and a yttria stabilized zirconia is applied to the intermediate silicon layer/coating. The matrix of a melt infiltrated silicon-silicon carbide (Si/SiC) composite comprises about 10-20 volume percent (vol%) residual silicon. This residual substrate silicon reduces the coefficient of thermal expansion (CTE) mismatch between the silicon-containing substrate and the silicon intermediate layer/coating. In this embodiment, the silicon intermediate layer/coating can be applied as an extension of the infiltration process in which excess silicon infiltrate is used to build up a silicon or silicon-rich layer/coating on the silicon-containing substrate's surface. Also, the silicon intermediate layer/coating can be applied by simply dipping the silicon-containing substrates into a silicon melt. Both applications provide a dense and uniform silicon layer/coating on the silicon-containing substrate's surface. The external environmental/thermal barrier coating can then be applied directly onto the intermediate silicon layer/coating without any major treatment. Preoxidation of the silicon layer/coating to form a top silicon oxide ( $\text{SiO}_2$ ) layer can improve bonding of oxide external barrier coatings. The intermediate layer/coating can also be applied by chemical vapor deposition (CVD), thermal spray, a solution based technique or other method.

**[0024]** When the external environmental/thermal barrier coating is an oxide that has a larger coefficient of thermal

expansion (CTE) than the silicon-containing substrate, stresses can arise during temperature changes such as during start-up or shut down or as a result of "hot-spots" in the coating at high temperatures (above about 1000°C). Thermal stresses are a main cause of coating failure and bond coat failure in these articles. The intermediate layer/coating of the invention is of particular advantage when used with these articles since it also serves as a stress-relieving compliant zone. Silicon deforms plastically at temperatures higher than about 600°C (while maintaining a shear strength over 10 Mpa). This plasticity reduces thermal stresses exerting on the layer/coating, and hence improves layer/coating life span.

[0025] In another aspect of the invention, the capability of an intermediate layer/coating can be customized to withstand a higher temperature diffused through an external barrier coating by using a silicon-alloy layer/coating or by adding a refractory second phase into a silicon intermediate layer/coating. Silicon-based refractories, silicon carbide (SiC) and silicon nitride ( $\text{Si}_3\text{N}_4$ ) can be used for this purpose so long as the proportion of silicon carbide (SiC) and silicon nitride ( $\text{Si}_3\text{N}_4$ ) is limited so that the purpose of eliminating gas generation is not defeated. Generally, the volume percent of silicon carbide (SiC) and silicon nitride ( $\text{Si}_3\text{N}_4$ ) should be limited to about 20 percent or less. Other non-gas generating refractory phases, such as silicon oxide ( $\text{SiO}_2$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ), may also be used provided that they do not deteriorate the oxidation resistance of the intermediate layer/coating.

[0026] Fiber-reinforced silicon carbide (SiC) matrix compositions can have a CVD silicon carbide (SiC) overcoat to protect the fibers and matrices. In accordance with the present invention, some or all of the silicon carbide (SiC) can be replaced with the silicon or silicon-alloy intermediate layer/coating. Silicon has a coefficient of thermal expansion (CTE) lower than that of silicon carbide (SiC). Hence, the intermediate layer/coating of the invention can comprise a graded layer/coating with higher silicon carbide (SiC) concentration at an intermediate layer/coating-substrate interface than at the interface between the intermediate layer/coating-external environmental/thermal barrier coating interface. The silicon concentration is greater toward the external environmental/thermal barrier coating-intermediate layer/coating interface than at the interface between the intermediate layer/coating-substrate interface. The final strata of the intermediate layer/coating will consist essentially of silicon. Codeposition of silicon and silicon carbide is possible, e.g., by controlling the hydrogen/silicon (H/Si) ratio when silicon tetrachloride ( $\text{CH}_3\text{SiCl}_3$ ) and hydrogen are used.

[0027] The following examples are for illustration of the invention only and do not limit the scope of the present invention.

#### EXAMPLE 1

[0028] In these examples, an intermediate layer/coating was applied to a silicon carbide (SiC) fiber-reinforced melt-infiltrated silicon-silicon carbide (Si-SiC) matrix. A 60  $\mu\text{m}$  thick silicon intermediate layer/coating was deposited at 1100°C with  $\text{SiCl}_2\text{H}_2$  and hydrogen for about 50 minutes at about 0.9 Torr pressure. A plasma mullite bond coat about 1-2 mil thick, was deposited with a plasma yttria stabilized zirconia top coat that was about 1 mil thick. The coating was subjected to oxidation testing at 1300°C for about 200 hours.

[0029] The results of comparison between the coatings with the silicon intermediate layer/coating and without the silicon intermediate layer/coating are shown in the SEM micrographs, where Figure 1 is without the silicon intermediate layer/coating and Figure 2 is with the silicon intermediate layer/coating.

[0030] After oxidation at 1300°C for 200 hours in air, the sample without the silicon intermediate layer/coating exhibited severe pore formation and debonding at the coating/substrate interface. The sample with the silicon intermediate layer/coating showed good bonding between the silicon intermediate layer/coating and silicon-containing substrate and between the silicon intermediate layer and external environmental/thermal barrier coating. No pore formation or debonding was seen at the coating-Si intermediate layer/coating interface.

#### EXAMPLE 2

[0031] In another example, a silicon intermediate layer/coating was applied by melt infiltration to the surface of a silicon carbide (SiC) fiber-reinforced melt infiltrated silicon-silicon carbide (Si-SiC) matrix composite. A yttria stabilized zirconia (YSZ)-mullite environmental/thermal barrier coating was applied to the intermediate silicon layer/coating. Figure 3 shows good bonding between all layers.

[0032] The Examples show that an intermediate silicon layer/coating can improve bonding and avoid the formation of gaseous oxidation products at an interface region between an environmental/thermal barrier coating (E/TBC) and a silicon-containing substrate.

#### Claims

1. An article, comprising:

a silicon-containing substrate that is oxidizable by reaction with an oxidant to at least one gaseous product; and an intermediate layer/coating applied onto said substrate, wherein said intermediate layer/coating is oxidizable to form a nongaseous product by reaction with said oxidant,

- 5        wherein (i) the intermediate layer/coating is silicon or a silicon-containing alloy or (ii) the intermediate layer/coating has a final strata that consists of silicon or a silicon-containing alloy.
2.    The article of claim 1, comprising a silicon-containing substrate and an external environmental/thermal barrier coating, wherein said external environmental/thermal barrier coating is permeable to diffusion of an environmental  
10       oxidant and said substrate is oxidizable by reaction with said oxidant to form at least one gaseous product; and an intermediate layer/coating between said substrate and said environmental /thermal barrier coating that is oxidizable to form a nongaseous product by reaction with said oxidant.
3.    The article of claim 1, wherein said substrate is silicon carbide or silicon nitride monolith or composite.  
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4.    The article of claim 2, wherein said external environmental/ thermal barrier coating comprises yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, magnesia-stabilized zirconia, alumina, alumina silicate or mixtures thereof.
- 20       5.    The article of claim 1, wherein said silicon containing alloy is selected from the group consisting of silicon aluminum (Si-Al), silicon chromium (Si-Cr), silicon magnesium (Si-Mg), silicon calcium (Si-Ca), silicon molybdenum (Si-Mo) and silicon titanium (Si-Ti).
- 25       6.    The article of claim 1, wherein said substrate comprises silicon carbide (SiC), silicon nitride (Si<sub>3</sub>N<sub>4</sub>), silicon carbide (SiC) fiber-reinforced silicon carbide (SiC matrix composite, carbon fiber-reinforced silicon carbide (SiC) matrix composite or a silicon carbide (SiC) fiber-reinforced silicon nitride (Si<sub>3</sub>N<sub>4</sub>) composite.
- 30       7.    The article of claim 1, wherein said substrate comprises a silicon carbide (SiC) fiber-reinforced silicon-silicon carbide (Si-SiC) matrix composite processed by silicon melt infiltration.
- 35       8.    The article of claim 2, comprising a silicon-containing substrate having a lower coefficient of thermal expansion than, the coefficient of thermal expansion of said external environmental/thermal barrier coating and said intermediate layer/coating reduces thermal stress between said substrate and said external environmental/ thermal barrier coating.
9.    The article of claim 8, wherein said intermediate layer/coating consists of silicon.
- 40       10.    The article of claim 2, wherein said substrate comprises silicon carbide (SiC) and said intermediate layer/coating comprises a graded layer/coating with higher silicon carbide (SiC) concentration at an intermediate layer/coating substrate interface than at an intermediate layer/coating external environmental/thermal barrier coating interface and increasing silicon concentration at an interface between the environmental/thermal barrier coating and the intermediate layer/coating.
- 45       11.    The article of claim 2, wherein said substrate is a silicon-based nonoxide ceramic matrix composition formed by silicon melt infiltration and said intermediate layer/coating is silicon.
- 50       12.    The article of claim 2, comprising a silicon carbide (SiC) fiber reinforced melt-infiltrated silicon-silicon carbide (Si-SiC) matrix substrate, a mullite-bonded yttria stabilized zirconia external environmental /thermal barrier coating and a silicon intermediate layer/coating.
- 55       13.    The article of claim 1 shaped into an engine part.
14.    The article of claim 1 comprising a silicon-containing substrate formed into a part and an external environmental/ thermal barrier coating, wherein said external barrier coating is permeable to diffusion of an environmental oxidant and said substrate is oxidizable by reaction with said oxidant to at least one gaseous product; and a continuous intermediate layer/coating between said substrate and said environmental/ thermal barrier coating that is oxidizable to form a nongaseous product by reaction with said oxidant in preference to reaction of said substrate with said oxidant.

15. The article of claim 4 where the external environmental /thermal barrier coating further comprises a bond coating.
16. The article of claim 15 where the bond coating comprises mullite, modified mullite or  $\text{MCrAlY}$  where M is nickel, iron, cobalt, or mixtures thereof.
17. The article of claim 16 where the mullite coating comprises a modifier component.
18. The article of claim 17 where the modifier component is selected from the group consisting of alkaline earth aluminosilicate having a formula  $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , where M is an alkaline earth element, yttrium silicates (YS), calcium aluminates, aluminum titanates, cordierite, fused silica, silicon,  $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ,  $\text{Ba}_{1.25}\text{Zr}_4\text{P}_5.5\text{Si}_{0.5024}\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4(\text{PO}_4)_6$ ,  $\text{Ca}_{0.6}\text{Mg}_{0.4}\text{Sr}_4(\text{PO}_4)_6$  and mixtures thereof.
19. The article of claim 18 where the formula  $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  includes barium feldspar ( $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), strontium feldspar ( $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), and combinations of barium feldspar ( $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), and strontium feldspar ( $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).
20. The article of claim 19 where the aluminosilicates include  $(\text{BaO})_{0.75}(\text{SrO})_{0.25} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (BSAS),  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (CAS) or combinations thereof.
21. The article of claim 1, comprising:  
     a silicon carbide (SiC) fiber-reinforced melt-infiltrated silicon-silicon carbide (Si-SiC) matrix substrate, a mullite bond coating, an yttria stabilized zirconia external environmental/ thermal barrier coating and a silicon intermediate layer/coating.
22. The article of claim 21 where the mullite coating comprises a modified component.
23. The article of claim 22 where modified component comprises  $(\text{BaO})_{0.75}(\text{SrO})_{0.25} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (BSAS),  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (CAS) or combinations thereof.
24. A method of forming an article, comprising;  
     forming a silicon-containing substrate that is oxidizable by reaction with an oxidant to at least one gaseous product;  
     and  
     applying an intermediate layer/coating onto said substrate, wherein said intermediate layer/coating is oxidizable to form a nongaseous product by reaction with said oxidant;  
     wherein (i) the intermediate layer/coating is silicon or a silicon-containing alloy or (ii) the intermediate layer/coating has a final strata that consists of silicon or a silicon-containing alloy.
25. The method of claim 24, comprising applying said intermediate layer/coating by chemical vapor deposition, melt infiltration, thermal spray or solution-based techniques.
26. The method of claim 24, further comprising applying an external environmental/ thermal barrier coating, onto said intermediate layer/coating, wherein said external environmental/ thermal barrier coating is permeable to diffusion of said oxidant.
27. The method of claim 26, wherein said substrate is a silicon carbide (SiC) substrate, comprising applying a silicon intermediate layer/coating onto said substrate to reduce thermal stress between said substrate and said external environmental /thermal barrier coating.
28. The method of claim 26, comprising applying said silicon intermediate layer/coating as a graded coating with higher silicon carbide (SiC) concentration at an intermediate layer/coating-substrate interface than at an intermediate layer/coating-external environmental/ thermal barrier coating interface and increasing silicon concentration at an interface between the environmental/ thermal barrier coating and the intermediate layer/coating.
29. The method of claim 26, wherein said substrate has a lower coefficient of thermal expansion than the coefficient of thermal expansion of said external environmental/ thermal barrier coating, comprising applying an intermediate layer/coating onto said substrate to reduce thermal stress between said substrate and said external environmental /thermal barrier coating.

30. The method of claim 29, wherein said intermediate layer/coating comprises silicon.

31. A method of improving the bond strength of the article of claim 1, comprising:

5 providing a silicon-based nonoxide substrate for application of an external environmental/ thermal barrier coating, wherein said external environmental/thermal barrier coating is permeable to diffusion of an environmental oxidant and said substrate is oxidizable by reaction with said oxidant to form at least one gaseous product; and applying an intermediate layer/coating onto said substrate, wherein said intermediate layer is oxidizable to a nongaseous product by reaction with said oxidant in preference to reaction of said substrate with said oxidant.

10 32. A method according to claim 24, comprising:

15 providing a silicon-silicon carbide substrate containing silicon carbide-containing fibers and said substrate having an external yttria stabilized zirconia coating; and applying a silicon intermediate layer/coating onto said substrate, wherein said intermediate layer is oxidizable to a nongaseous product by reaction with said oxidant in preference to reaction of said substrate with said oxidant.

20 33. A method according to claim 32 where the external environmental/ thermal barrier coating further comprises a bond coat.

34. A method according to claim 33 where the bond coat is mullite, modified mullite or MCrAlY where M is nickel, iron, cobalt, or mixtures thereof.

25 35. A method according to claim 34 where the mullite coating comprises a modifier component.

## Revendications

30 1. Article comprenant :

un substrat contenant du silicium qui peut être oxydé en au moins un produit gazeux par réaction avec un oxydant ; et  
35 une couche intermédiaire appliquée sur ledit substrat, dans lequel ladite couche intermédiaire peut être oxydée pour former un produit non gazeux par réaction avec ledit oxydant,

dans lequel (i) la couche intermédiaire est du silicium ou un alliage contenant du silicium, ou (ii) la couche intermédiaire présente une dernière couche constituée de silicium ou d'un alliage contenant du silicium.

40 2. Article selon la revendication 1, qui comprend un substrat contenant du silicium et un revêtement externe barrière contre la chaleur/environnement, dans lequel ledit revêtement externe barrière contre la chaleur/environnement est perméable à la diffusion d'un oxydant de l'environnement et ledit substrat peut être oxydé par réaction avec ledit oxydant pour former au moins un produit gazeux ; et  
45 une couche intermédiaire entre ledit substrat et ledit revêtement externe barrière contre la chaleur/environnement, qui peut être oxydé pour former un produit non gazeux par réaction avec ledit oxydant.

3. Article selon la revendication 1, dans lequel ledit substrat est du carbure de silicium ou un monolithe de nitrure de silicium ou un composite.

50 4. Article selon la revendication 2, dans lequel ledit revêtement externe barrière contre la chaleur/environnement comprend de l'oxyde de zirconium stabilisé avec de l'oxyde d'yttrium, de l'oxyde de zirconium stabilisé avec de l'oxyde de scandium, de l'oxyde de zirconium stabilisé avec de l'oxyde de calcium, de l'oxyde de zirconium stabilisé avec de l'oxyde magnésium, de l'alumine, du silicate d'alumine ou leurs mélanges.

55 5. Article selon la revendication 1, dans lequel ledit alliage contenant du silicium est choisi dans l'ensemble constitué par du silicium-aluminium (Si-Al), du silicium-chrome (Si-Cr), du silicium-magnésium (Si-Mg), du silicium-calcium (Si-Ca), du silicium-molybdène (Si-Mo) et du silicium-titane (Si-Ti).



6. Article selon la revendication 1, dans lequel ledit substrat comprend du carbure de silicium (SiC), du nitrure de silicium ( $\text{Si}_3\text{N}_4$ ), un composite à matrice carbure de silicium (SiC) renforcé avec des fibres de carbure de silicium (SiC), un composite à matrice carbure de silicium (SiC) renforcée avec des fibres de carbone, ou un composite de nitrure de silicium ( $\text{Si}_3\text{N}_4$ ) renforcé avec des fibres de carbure de silicium (SiC).
7. Article selon la revendication 1, dans lequel ledit substrat comprend un composite à matrice silicium-carbure de silicium (Si-SiC) renforcée avec des fibres de carbure de silicium (SiC), traité par infiltration à l'état fondu de silicium.
8. Article selon la revendication 2, qui comprend un substrat contenant du silicium et présentant un coefficient de dilatation thermique inférieur au coefficient de dilatation thermique dudit revêtement externe barrière contre la chaleur/environnement, et ladite couche intermédiaire réduit la tension thermique entre ledit substrat et ledit revêtement externe barrière contre la chaleur/environnement.
9. Article selon la revendication 8, dans lequel ladite couche intermédiaire est constituée de silicium.
10. Article selon la revendication 2, dans lequel ledit substrat comprend du carbure de silicium (SiC) et ladite couche intermédiaire comprend une couche à gradient présentant une concentration de carbure de silicium (SiC) plus élevée à l'interface couche intermédiaire/substrat que celle à l'interface couche intermédiaire/revêtement externe barrière contre la chaleur/environnement, et une concentration croissante de silicium à l'interface entre le revêtement externe barrière contre la chaleur/environnement et la couche intermédiaire.
11. Article selon la revendication 2, dans lequel ledit substrat est une composition à matrice céramique de nonoxyde à base de silicium, formée par infiltration à l'état fondu de silicium et ladite couche intermédiaire est du silicium.
12. Article selon la revendication 2, comprenant un substrat à matrice silicium-carbure de silicium (Si-SiC) infiltrée à l'état fondu et renforcée avec des fibres de carbure de silicium (SiC), un revêtement externe barrière contre la chaleur/environnement à base d'oxyde de zirconium stabilisé avec l'oxyde d'yttrium, lié avec de la mullite, et une couche intermédiaire de silicium.
13. Article selon la revendication 1, sous la forme d'une pièce moteur.
14. Article selon la revendication 1, comprenant un substrat contenant du silicium sous la forme d'une pièce, et un revêtement externe barrière contre la chaleur/environnement, dans lequel ledit revêtement externe barrière est perméable à la diffusion d'un oxydant de l'environnement et ledit substrat peut être oxydé en au moins un produit gazeux par réaction avec ledit oxydant ; et une couche intermédiaire continue entre ledit substrat et ledit revêtement externe barrière contre la chaleur/environnement qui peut être oxydé pour former un produit non gazeux par réaction avec ledit oxydant, qui est préférée à la réaction entre ledit substrat et ledit oxydant.
15. Article selon la revendication 4, dans lequel le revêtement externe barrière contre la chaleur/environnement comprend en outre un revêtement de liaison.
16. Article selon la revendication 15, dans lequel le revêtement de liaison comprend de la mullite, de la mullite modifiée ou  $\text{MCrAlY}$  où M représente le nickel, le fer, le cobalt ou leur mélanges.
17. Article selon la revendication 16, dans lequel le revêtement de mullite comprend un composant de modification.
18. Article selon la revendication 17, dans lequel le composant de modification est choisi dans l'ensemble constitué par les aluminosilicates de métal alcalino-terreux répondant à la formule  $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , où M représente un métal alcalino-terreux, des silicates d'yttrium (YS), des aluminates de calcium, des titanates d'aluminium, la cordiérite, la silice pyrogénée, du silicium,  $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ,  $\text{Ba}_{1,25}\text{Zr}_4\text{P}_{5,5}\text{Si}_{0,5}\text{O}_{24}$ ,  $\text{Ca}_{0,5}\text{Sr}_{0,5}\text{Zr}_4(\text{PO}_4)_6$ ,  $\text{Ca}_{0,6}\text{Mg}_{0,4}\text{Sr}_4(\text{PO}_4)_6$  et leurs mélanges.
19. Article selon la revendication 18, dans lequel la formule  $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  comprend le feldspath de baryum ( $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), le feldspath de strontium ( $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), et les combinaisons de feldspath de baryum ( $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) et de feldspath de strontium ( $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).
20. Article selon la revendication 19, dans lequel les aluminosilicates comprennent  $(\text{BaO})_{0,75}(\text{SrO})_{0,25} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (BSAS),  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (CAS) ou leurs combinaisons.

21. Article selon la revendication 1, comprenant :

un substrat à matrice silicium-carbure de silicium (Si-SiC) infiltrée à l'état fondu et renforcée avec des fibres de carbure de silicium (SiC), un revêtement de liaison de mullite, un revêtement externe barrière contre la chaleur/environnement à base d'oxyde de zirconium stabilisé avec de l'oxyde d'yttrium, et une couche intermédiaire de silicium.

22. Article selon la revendication 21, dans lequel le revêtement de mullite comprend un composant de modification.

23. Article selon la revendication 22, dans lequel un composant de modification comprend  $(\text{BaO})_{0,75}(\text{SrO})_{0,25} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (BSAS),  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (CAS) ou leurs combinaisons.

24. Procédé de formation d'un article, comprenant :

la formation d'un substrat contenant du silicium qui peut être oxydé en au moins un produit gazeux par réaction avec un oxydant ;  
l'application d'une couche intermédiaire appliquée sur ledit substrat, dans lequel ladite couche intermédiaire peut être oxydée pour former un produit non gazeux par réaction avec ledit oxydant ;

dans lequel (i) la couche intermédiaire est du silicium ou un alliage contenant du silicium, ou (ii) la couche intermédiaire présente une dernière couche constituée de silicium ou d'un alliage contenant du silicium.

25. Procédé selon la revendication 24, comprenant l'application de ladite couche intermédiaire par dépôt chimique en phase vapeur, infiltration à l'état fondu, pulvérisation thermique ou des techniques basées sur des solutions.

26. Procédé selon la revendication 24, comprenant en outre l'application d'un revêtement externe barrière contre la chaleur/environnement sur ladite couche intermédiaire, dans lequel ledit revêtement externe barrière contre la chaleur/environnement est perméable à la diffusion dudit oxydant.

27. Procédé selon la revendication 26, dans lequel ledit substrat est un substrat de carbure de silicium (SiC), comprenant l'application d'une couche intermédiaire de silicium sur ledit substrat pour réduire une tension thermique entre ledit substrat et ledit revêtement externe barrière contre la chaleur/environnement.

28. Procédé selon la revendication 26, comprenant l'application d'une couche intermédiaire comme revêtement à gradient présentant une concentration de carbure de silicium (SiC) plus élevée à l'interface couche intermédiaire/substrat que celle à l'interface couche intermédiaire/revêtement externe barrière contre la chaleur/environnement, et une concentration croissante de silicium à l'interface entre le revêtement barrière contre la chaleur/environnement externe et la couche intermédiaire.

29. Procédé selon la revendication 26, dans lequel ledit substrat présente un coefficient de dilatation thermique inférieur au coefficient de dilatation thermique dudit revêtement externe barrière contre la chaleur/environnement, comprenant l'application d'une couche intermédiaire sur ledit substrat pour réduire la tension thermique entre ledit substrat et ledit revêtement externe barrière contre la chaleur/environnement.

30. Procédé selon la revendication 29, dans lequel ladite couche intermédiaire comprend du silicium.

31. Procédé pour améliorer la résistance d'adhérence de l'article selon la revendication 1, comprenant :

la fourniture d'un substrat de nonoxyde à base de silicium pour appliquer un revêtement externe barrière contre la chaleur/environnement, dans lequel ledit revêtement externe barrière contre la chaleur/environnement est perméable à la diffusion d'un oxydant de l'environnement et ledit substrat peut être oxydé par réaction avec ledit oxydant pour former au moins un produit gazeux ; et  
l'application d'une couche intermédiaire sur ledit substrat, dans lequel ladite couche intermédiaire peut être oxydée en un produit non gazeux par réaction avec ledit oxydant, qui est préférée à la réaction entre ledit substrat et ledit oxydant.

32. Procédé selon la revendication 24, comprenant la fourniture d'un substrat silicium-carbure de silicium qui contient des fibres comprenant du carbure de silicium,

ledit substrat présentant un revêtement externe d'oxyde de zirconium stabilisé avec de l'oxyde d'yttrium ; et l'application d'une couche intermédiaire de silicium sur ledit substrat, dans lequel ladite couche intermédiaire peut être oxydée en un produit non gazeux par réaction avec ledit oxydant, qui est préférée à la réaction entre ledit substrat et ledit oxydant.

33. Procédé selon la revendication 32, dans lequel le revêtement externe barrière contre la chaleur/environnement comprend en outre un revêtement de liaison.

34. Procédé selon la revendication 33, dans lequel le revêtement de liaison est de la mullite, de la mullite modifiée ou  $\text{MCrAlY}$  où M représente le nickel, le fer, le cobalt ou leur mélanges.

35. Procédé selon la revendication 34, dans lequel le revêtement de mullite comprend un composant de modification.

## Patentansprüche

### 1. Gegenstand enthaltend:

ein Silizium enthaltendes Substrat, das durch Reaktion mit einem Oxidationsmittel in wenigstens ein gasförmiges Produkt oxidierbar ist, und eine Zwischenschicht/Überzug, die auf das Substrat aufgebracht ist, wobei die Zwischenschicht/Überzug zum Bilden eines nicht-gasförmigen Produktes durch Reaktion mit dem Oxidationsmittel oxidierbar ist,

wobei (i) die Zwischenschicht/Überzug Silizium oder eine siliziumhaltige Legierung ist oder (ii) die Zwischenschicht/Überzug eine Endsicht hat, die aus Silizium oder einer siliziumhaltigen Legierung besteht.

2. Gegenstand nach Anspruch 1, enthaltend ein siliziumhaltiges Substrat und einen Aussenumgebungs/thermischen Trennüberzug, wobei der Aussenumgebungs/thermische Überzug gegenüber Diffusion eines Umgebungs-Oxidationsmittels permeabel ist und das Substrat durch Reaktion mit dem Oxidationsmittel oxidierbar ist, um wenigstens ein gasförmiges Produkt zu bilden, und eine Zwischenschicht/Überzug zwischen dem Substrat und dem Aussenumgebungs/thermischen Überzug, der oxidierbar ist zum Bilden eines nicht-gasförmigen Produktes durch Reaktion mit dem Oxidationsmittel.

3. Gegenstand nach Anspruch 1, wobei das Substrat Siliziumkarbid oder Siliziumnitrid-Monolith oder -Verbundkörper ist.

4. Gegenstand nach Anspruch 2, wobei Aussenumgebungs/ thermische Trennüberzug Yttriumoxid-stabilisiertes Zirkonoxid, Scandiumoxid-stabilisiertes Zirkonoxid, Kalziumoxid-stabilisiertes Zirkonoxid, Magnesiumoxid-stabilisiertes Zirkon, Aluminiumoxid, Aluminiumoxid-Silikat oder Mischungen davon aufweist.

5. Gegenstand nach Anspruch 1, wobei die siliziumhaltige Legierung aus der aus Silizium-Aluminium (Si-Al), Silizium-Chrom (Si-Cr), Silizium-Magnesium (Si-Mg), Silizium-Kalzium (Si-Ca), Silizium-Molybdän (Si-Mo) und Silizium-Titan (Si-Ti) bestehenden Gruppe ausgewählt ist.

6. Gegenstand nach Anspruch 1, wobei das Substrat Siliziumkarbid (SiC), Siliziumnitrid ( $\text{Si}_3\text{N}_4$ ), Siliziumkarbidfaser-verstärkten Siliziumkarbid (SiC)-Matrixverbund, Kohlefaserverstärkten Siliziumkarbid (SiC)-Matrixverbund oder Siliziumkarbid(SiC)faser-verstärkten Siliziumnitrid( $\text{Si}_3\text{N}_4$ )-Matrixverbund enthält.

7. Gegenstand nach Anspruch 1, wobei das Substrat Siliziumkarbid(SiC)faser-verstärkten Siliziumkarbid(Si-SiC) Matrixverbund aufweist, der durch Silizium-Schmelzinfiltration hergestellt ist.

8. Gegenstand nach Anspruch 2, enthaltend ein siliziumhaltiges Substrat, das einen kleineren thermischen Ausdehnungskoeffizienten als den thermischen Ausdehnungskoeffizienten des Aussenumgebung/thermischen Überzug hat, und die Zwischenschicht/Überzug die thermische Beanspruchung zwischen dem Substrat und der Aussenumgebung/thermischen Überzug senkt.

9. Gegenstand nach Anspruch 8, wobei die Zwischenschicht/Überzug aus Silizium besteht.

10. Gegenstand nach Anspruch 2, wobei das Substrat Siliziumkarbid (SiC) aufweist und die Zwischenschicht/Überzug eine abgestufte Schicht/Überzug mit höherer Siliziumkarbid(SiC)-Konzentration an einer Zwischenschicht/Überzug-Substratgrenzfläche als an einer Zwischenschicht/Überzug-Aussen-Umgebungs/thermischen Trennüberzug-grenzfläche aufweist und die Silizium-Konzentration an der Grenzfläche zwischen dem Aussenumgebung/thermischer Überzug und der Zwischenschicht/Überzug ansteigt.
11. Gegenstand nach Anspruch 2, wobei das Substrat eine Siliziumbasis-Nichtoxid-keramikmatrixzusammensetzung ist, die durch Siliziumschmelze-Infiltration gebildet ist, und die Zwischenschicht/Überzug Silizium ist.
12. Gegenstand nach Anspruch 2, enthaltend ein Siliziumkarbid (SiC) faser-verstärktes, schmelzinfiltriertes Silizium-Siliziumkarbid (Si-SiC) -Matrixsubstrat, einen Mullit-gebundenen Yttriumoxid-stabilisierten Zirkonoxid-Aussenumgebungs/thermischen Trennüberzug und einen Silizium-Zwischenschicht/Überzug.
13. Gegenstand nach Anspruch 1, der zu einem Triebwerksteil geformt ist.
14. Gegenstand nach Anspruch 1, enthaltend ein silizium-haltiges Substrat, das zu einem Teil geformt ist, und einen Aussenumgebungs/thermischen Trennüberzug, wobei der äussere Trennüberzug gegenüber Diffusion eines Umgebungs-Oxidations-mittels permeabel ist und das Substrat durch Reaktion mit dem Oxidations-mittel zu wenigstens einem gasförmigen Produkt oxidierbar ist; und eine kontinuierliche Zwischenschicht/Überzug zwischen dem Substrat und dem Aussenumgebung/thermischer Überzug, der oxidierbar ist zum Bilden eines nicht-gasförmigen Produktes durch Reaktion mit dem Oxidationsmittel bevorzugt zu einer Reaktion des Substrates mit dem Oxidationsmittel.
15. Gegenstand nach Anspruch 4, wobei der Aussenumgebung/thermische Überzug ferner einen Bindungsüberzug aufweist.
16. Gegenstand nach Anspruch 15, wobei der Bindungsüberzug Mullit, modifiziertes Mullit oder MCrAlY aufweist, wobei M Nickel, Eisen, Kobalt oder Mischungen davon ist.
17. Gegenstand nach Anspruch 16, wobei der Mullitüberzug eine Modifiziererkomponente aufweist.
18. Gegenstand nach Anspruch 17, wobei die Modifiziererkomponente aus der aus Erdalkali-Alumino-Silikat mit der Formel  $MO \cdot Al_2O_3 \cdot 2SiO_2$  bestehenden Gruppe ausgewählt ist, wobei M ein Erdalkalielement, Yttrium-Silikate (YS), Kalzium-Aluminate, Aluminium-Titanate, Cordierit, gebranntes Siliziumdioxid,  $NaZr_2P_3O_{12}$ , Rest  $0,25Zr_4P_5,5SiO_{5024}$ ,  $Ca_{0,5}Sr_{0,5}Zr_4(PO_4)_6$ ,  $Ca_{0,6}Mg_{0,4}Sr_4(P_4O_{14})_6$  und Mischungen davon ist.
19. Gegenstand nach Anspruch 18, wobei die Formel  $MO \cdot Al_2O_3 \cdot 2SiO_2$  Barium-Feldspat ( $BaO \cdot Al_2O_3 \cdot 2SiO_2$ ), Strontium-Feldspat ( $SrO \cdot Al_2O_3 \cdot 2SiO_2$ ) und Kombinationen von Barium-Feldspat ( $BaO \cdot Al_2O_3 \cdot 2SiO_2$ ) und Strontium-Feldspat ( $SrO \cdot Al_2O_3 \cdot 2SiO_2$ ) enthält.
20. Gegenstand nach Anspruch 19, wobei die Alumino-Silikate  $(BaO)_{0,75}(SrO)_{0,25} \cdot Al_2O_3 \cdot 2SiO_2$  (BSAS),  $CaO \cdot Al_2O_3 \cdot 2SiO_2$  (CAS) oder Kombinationen davon enthalten.
21. Gegenstand nach Anspruch 1, enthaltend:  
ein Siliziumkarbid(SiC)faser-verstärktes, schmelzinfiltriertes Silizium-Siliziumkarbid(Si-SiC)-Matrixsubstrat, einen Mullit-Bindungsüberzug, einen Yttriumoxid-stabilisierten Zirkonoxid-Aussenumgebungs/thermischen Trennüberzug und eine Siliziumzwischenschicht/Überzug.
22. Gegenstand nach Anspruch 21, wobei der Mullit-Überzug eine modifizierte Komponente aufweist.
23. Gegenstand nach Anspruch 22, wobei die modifizierte Komponente  $(BaO)_{0,75}(SrO)_{0,25} \cdot Al_2O_3 \cdot 2SiO_2$  (BSAS),  $CaO \cdot Al_2O_3 \cdot 2SiO_2$  (CAS) oder Kombinationen davon enthält.
24. Verfahren zum Bilden eines Gegenstandes, enthaltend:  
Bilden eines Silizium enthaltenden Substrats, das durch Reaktion mit einem Oxidationsmittel zu wenigstens einem gasförmigen Produkt oxidierbar ist, und

Aufbringen einer Zwischenschicht/überzugs auf das Substrat,

wobei die Zwischenschicht/überzug zum Bilden eines nicht-gasförmigen Produktes durch Reaktion mit dem Oxidationsmittel oxidierbar ist,

wobei (i) die Zwischenschicht/überzug Silizium oder eine siliziumhaltige Legierung ist oder (ii) die Zwischenschicht/überzug eine Endschrift hat, die aus Silizium oder einer siliziumhaltigen Legierung besteht.

25. Verfahren nach Anspruch 24, enthaltend Aufbringen der Zwischenschicht/überzugs durch chemische Dampfab-scheidung, Schmelzinfiltration, thermisches Sprühen oder Lösungs-basierte Techniken.

26. Verfahren nach Anspruch 24, ferner enthaltend Aufbringen eines Aussenumgebungs/thermischen Überzugs auf den Zwischenschicht/überzug, wobei der Aussenumgebung/thermische Überzug gegenüber Diffusion des Oxi-dationsmittels permeabel ist.

27. Verfahren nach Anspruch 26, wobei das Substrat Siliziumkarbid(SiC)-Substrat ist, enthaltend Aufbringen einer Siliziumzwischenschicht/überzug auf das Substrat, um die thermische Beanspruchung zwischen dem Substrat und dem Aussenumgebung/thermischen Überzug verringern.

28. Verfahren nach Anspruch 26, enthaltend Aufbringen des Siliziumzwischenschicht/überzugs als einen abgestuften Überzug mit höherer Siliziumkarbid(SiC)-Konzentra-tion an einer Zwischenschicht/Überzug-Substratgrenzfläche als an einer Zwischenschicht/Überzug-Aussenumge-bungs/thermischen Trennüberzuggrenzfläche und Vergrössern der Silizium-Konzentration an einer Grenzfläche zwischen dem Aussenumgebung/thermischen Überzug und der Zwischenschicht/Überzug.

29. Verfahren nach Anspruch 26, wobei das Substrat einen kleineren thermischen Ausdehnungskoeffizienten als den thermischen Ausdehnungskoeffizienten des Aussenumgebung/thermischer Überzugs hat, enthaltend Aufbringen eines Zwischenschicht/überzugs auf das Substrat, um die thermische Beanspruchung zwischen dem Substrat und dem Aussenumgebung/thermischen Überzug verringern.

30. Verfahren nach Anspruch 29, wobei die Zwischenschicht/überzug Silizium aufweist.

31. Verfahren zum Verbessern der Bindefestigkeit des Gegenstandes nach Anspruch 1, enthaltend:

Bereitstellen eines Silizium-basierten Nichtoxid-Substrates zum Aufbringen eines Aussenumgebung/thermi-schen Überzugs, wobei der Aussenumgebungs/thermischer Überzug gegenüber einer Diffusion eines Umge-bungs-Oxidationsmittels permeabel ist, und das Substrat oxidierbar ist Reaktion mit dem Oxidationsmittel, um wenigstens ein gasförmiges Produkt zu bilden, und Aufbringen einer Zwischenschicht/überzug auf das Substrat, wobei die Zwischenschicht zu einem nicht-gas-förmigen Produkt oxidierbar ist durch Reaktion mit dem Oxidationsmittel bevorzugt zu einer Reaktion des Substrates mit dem Oxidationsmittel.

32. Verfahren nach Anspruch 24, enthaltend:

Bereitstellen eines Silizium-Siliziumkarbid-Substrates, das Siliziumkarbid enthaltende Fasern enthält, und das Substrat einen äusseren Yttriumoxid-stabilisierten Zirkonoxid-Überzug hat, wobei die Zwischenschicht zu ei-nem nicht-gasförmigen Produkt oxidierbar ist durch Reaktion mit dem Oxidationsmittel bevorzugt zu einer Reaktion des Substrates mit dem Oxidationsmittel.

33. Verfahren nach Anspruch 32, wobei der Aussenumgebung/thermische Überzug ferner einen Bindungsüberzug aufweist.

34. Verfahren nach Anspruch 33, der Bindungsüberzug Mullit, modifiziertes Mullit oder MCrAlY aufweist, wobei M Nikkel, Eisen, Kobalt oder Mischungen davon ist.

35. Verfahren nach Anspruch 34, wobei der Mullitüberzug eine Modifiziererkomponente aufweist.



F16.3



FIG. 1

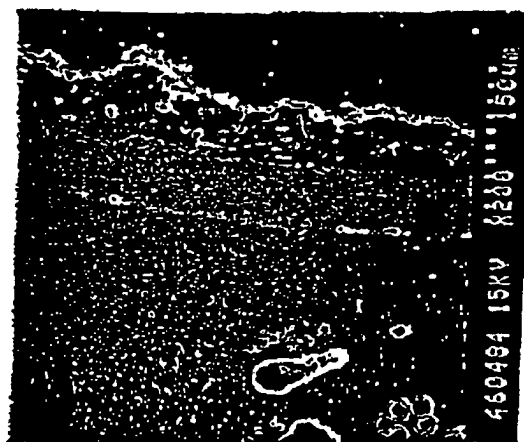


FIG. 2